



FIG. 4: Effects of small magnetic fields on fully labeled acetonitrile  $^{13}\text{CH}_3^{13}\text{C}^{15}\text{N}$ . The bottom trace shows the entire zero-field spectrum. The upper traces show an expanded view of the central part of the zero-field spectrum, as well as the spectra in the indicated finite fields.

with a  $^{13}\text{CH}_3$  group, and confine our attention to the  $1 \leftrightarrow 0$  transition with total proton spin  $= 1/2$ , yielding transitions in the neighborhood of  $^1J_{\text{CH}}$ . Addition of the second  $^{13}\text{C}$  splits these levels:  $f = 1$  splits to  $3/2$ ,  $1/2$  manifolds, and  $f = 0$  manifolds splits to  $1/2$ . Addition of the  $^{15}\text{N}$  splits these so we now have  $f_a = 2$  or  $1$ ,  $f_b = 1$  or  $0$ , and  $f_c = 1$  or  $0$ . For now, we ignore transitions between  $f_a \leftrightarrow f_b$  because they occur at low frequency. Employing the  $\Delta f = 1$  rule we expect three  $1 \leftrightarrow 0$  transitions, producing doublets:  $f_a = 1 \leftrightarrow f_c = 0$ ,  $f_b = 1 \leftrightarrow f_c = 0$ , and  $f_b = 0 \leftrightarrow f_c = 1$ . Transitions between  $f_a = 2 \leftrightarrow f_c = 1$  yields a multiplet with six lines, and transitions with  $\Delta f = 0$  between  $f_a = 1 \leftrightarrow f_c = 1$  and between  $f_b = 1 \leftrightarrow f_c = 1$  yield multiplets with four lines. More details are presented in the Supplementary Information.

In systems with small couplings, such as 1-acetic acid ( $\text{CH}_3^{13}\text{COOH}$ ) which has a two-bond coupling,  $^2J_{\text{CH}} = 6.8$  Hz, it is possible to explore the regime in which the Zeeman interaction is comparable to the  $J$ -coupling. Figure 5 shows experimental spectra for 1-acetic acid for the indicated magnetic fields. The large peak that does not split is due to the uncoupled OH group, while the rest of the spectrum corresponds to the  $\text{CH}_3^{13}\text{C}$  part of the molecule. Initially, the spectrum appears similar to the 2-acetonitrile spectrum, with a doublet at  $J$ , and an additional doublet at  $2J$  composed of several unresolved lines. As the magnetic field is increased, additional lines in the multiplet at  $2J$  become resolved. At the highest magnetic fields, the spectrum displays the highest complexity, and is no longer recognizable from the perturbative treatment presented above. The smooth trace at the